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Internal Chemical Bonding in Solutions of Simple Phosphates and Vanadates[†]

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ABSTRACT: The chemical bonding within structurally related phosphates and vanadates in aqueous solution is compared on the basis of vibrational frequencies obtained by classical Raman spectroscopy. To do this, an empirical relationship between the stretching frequency of P∸O and P∸OH or P∸OR groups and bond strength is developed such that the sum of the PO bond strengths, expressed in terms of average number of electron pairs per bond, is as close as possible to 5.0 for phosphoric acid and various anions and esters thereof. The same approach is used for the corresponding vanadates. The internal bonding in phosphates involves a greater bond strength for P∸OH and a smaller strength for P∸O than might be expected from a simple consideration of canonical resonance forms. In vanadates, V∸OH and V∸O are closer to single and double bonds, respectively, than in phosphates, and the force constant for V═O is considerably smaller than for P═O, although that for V—OH and P—OH is similar. Since treating the P∸O and V∸O groups of simple tetrahedral phosphates and vanadates as independent diatomic oscillators provides good correlations between the respective frequencies and bond strengths, the same correlations are used to approximate the expected stretching frequencies for distorted phosphates and vanadates. The distortions considered are those that presumably characterize associative and dissociative transition states for a concerted transfer of the (PO_3^-) fragment of a dianionic phosphate group between donor and acceptor oxygens with similar character. The results are compared with measured frequencies for ground-state and transition-state analog complexes of phosphoglucomutase in the accompanying paper [Deng, H., Ray, W. J., Jr., Burgner, J. W., II, & Callender, R. (1993) *Biochemistry* (following paper in this issue)].

Vanadate frequently acts as a phosphate analog in enzymic reactions, and its physical/chemical similarity to phosphate is noted frequently [*cf.* Gresser and Tracey (1990) and Rehder (1992), and references therein]. This similarity is particularly obvious in the respective trianions, where the tetrahedral arrangement of V—O bonds involves bond lengths only about 0.15 Å longer (Holloway & Melnik, 1986) than the P—O bonds in PO_4^{3-} [Corbridge, 1990; see also Shannon and Calvo (1973)]. However, chemical similarities between vanadates and the corresponding phosphates diverge, increasingly, in the slightly basic to neutral pH range, as one and then two V∸O groups are protonated.[1] This divergence is emphasized by the plethora of polynuclear polymers with V—O—V bonds that are stable in the neutral pH range (Habayeeb & Hillman, 1980; Heath & Howarth, 1981)—polymers that frequently plague studies where the objective is a comparison of vanadates with structurally similar phosphates.[2]

One objective of the present study is to quantify an experimental approach for comparing phosphates and vanadates. To do this, we assess the internal bonding in the various ionic forms of model compounds, primarily in aqueous solution, on the basis of a derived relationship between vibrational frequency and bond strength (see below), based on the spectroscopic view of bonds as harmonic oscillators. (Within this context, bond strength thus is a measure of the force constant that characterizes a bond in the ground state, as opposed to bond dissociation energy, which is a different measure of bond strength.) Thus, it has been known for some time that the characteristic frequency for the constituent P∸O bonds of phosphates differs in the various ions [*cf.* Corbridge (1969)], since both the symmetric and asymmetric P∸O stretching frequencies, υ_s and υ_a,[3] respectively, increase substantially as three protons are bound successively to PO_4^{3-} [*cf.* Zwick *et al.* (1989) and Results]. For diatomic oscillators, frequency differences usually can be correlated with differences in the bond strength factor of Gordy's equation (Gordy, 1946), which in turn is based on Badger's relationship (Badger, 1935).[4] The bond strength factor in both is equal to the average number of electron pairs participating in the bond and thus is related to Pauling's original definition of bond strength (Pauling, 1929).[5] The attractiveness of Gordy's equation, and modifications thereof, is that it involves rather basic empirical concepts such as force constant, reduced mass, and electronegativity differences. Moreover, a single parameter set

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[1] Abbreviations/symbols: υ_a, υ_s, and υ_ω, asymmetric, symmetric, and fundamental vibrational frequency, respectively; *s*, bond strength defined so that it represents the average number of electron pairs involved in a bond, *viz.*, so that the summed bond strengths for an atom are equal to its oxidation state, or valence; vu, valence units; ∸ [as in P∸O and P∸OH (or P∸O(H) when referring to both)], bonds whose strength is likely between 1 and 2; — and ═, bonds assumed to involve one and two pairs of electrons, respectively; ··, bonds whose strength is less than 1.

[2] Although such polymers are far more stable, thermodynamically, than pyrophosphate, for example, in some cases their kinetic stability is enormously less, and equilibrium depolymerization usually is achieved rapidly on dilution of neutral to basic solutions.

[3] The relationship between symmetric, antisymmetric, and fundamental stretching frequencies, υ_s, υ_a, and υ_ω, respectively, is $(n + 1)\upsilon_\omega^2 = \upsilon_s^2 + n\upsilon_a^2$, where *n* is the degeneracy of the antisymmetric modes (when these are present; Wilson *et al.*, 1955. In the present paper, when there are no antisymmetric modes, *e.g.*, in the case of the P∸O group of $(HO)_3PO$, the stretching mode is a fundamental mode; however, in such cases measured values are listed in Tables under υ_s rather than under the separate heading of υ_ω. See also Corbridge (1969) for diagrams defining υ_s and υ_a for phosphates.

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correlates frequency with bond strength for a variety of diatomic molecules. For more complex molecules, such as phosphates, the same basic relationship can be used, but arbitrary parameter adjustments are required to obtain reasonable values of bond strength (Gordy, 1946), and reported bond strengths for such molecules depend on how scaling factors are chosen. For vanadates, where bond strengths vary widely [the length of the V$\overset{\cdot\cdot}{-}$O bond can range almost continuously from about 1.56 to 2.8 Å (Holloway & Melnik, 1986)], even incorporating arbitrary scaling factors into Gordy's equation does not produce an expression that applies to the entire range of bond strengths (Hardcastle & Wachs, 1991) (although a scaled version of Gordy's equation provides a good correlation for both vanadates and phosphates over a more limited range; see Results).

A more basic approach to bond strengths utilizes crystallographic bond lengths (Brown & Wu, 1976; Brown, 1978). When bond strengths evaluated in this way are scaled according to network theory so that the sum of the bond strengths for each atom in a crystal is equal to its formal oxidation state, valence, or shared electron pairs, the bond strength value is referred to as bond valence (Brown, 1992). The first attempt, of which we are aware, to formulate a relationship between bond valence and Raman frequency of complex entities involved a study of 92 different VO bonds in 14 crystals and two liquids for which bond distances were available (Hardcastle & Wachs, 1991). The results of that study and the general success of the bond valence paradigm in providing a basis for rationalizing a plethora of phenomena (Brown & Shannon, 1973; Brown, 1978, 1980, 1987, 1992) encouraged us to attempt a formulation of a spectroscopic bond strength–frequency relationship that could be used both to compare the internal bonding of phosphates and vanadates in aqueous solution and to assess the internal bonding of PO and VO bonds in phosphoglucomutase, as well as in some of its substrate and inhibitor complexes.

In our approach we follow the bond valence convention cited above and impose the constraint that the sum of the spectroscopic bond strengths for PO bonds in phosphates and VO bonds in vanadates be as close as possible to 5.0. Because of this scaling choice we report our bond strengths, like bond valences, in terms of valence units (vu). However, the fact that we do not have solution values for PO and VO distances and do not utilize network theory in our approach differentiates our bond strengths from true bond valences. Ideally, spectroscopic bond strengths should be the same as bond valences obtained from a solution version of the bond valence paradigm (Brown, 1992), and in general the agreement is good (see Discussion). Nevertheless, we maintain the above distinction to emphasize the difference in our approach and that of Brown and co-workers.

Although many stretching frequency guides have been posed for distinguishing among $>$PO, $>PO_2^-$, and $-PO_3^{2-}$ groups in various phosphorus compounds [*cf.* Corbridge (1990)], to our knowledge, no previous attempt has been made to construct a bond strength scale for P$\overset{\cdot\cdot}{-}$O and P$\overset{\cdot\cdot}{-}$OH groups on the basis of stretching frequencies. Moreover, although Hardcastle and Wachs (1991) considered two liquid VO compounds, no attempt has been made to establish a similar frequency–bond strength correlation for simple vanadates in aqueous solution. Our approach to this problem is related to that of Hardcastle and Wachs (1991), but the procedure for assignment of bond strengths is different. Thus, although solution values for bond lengths of P$\overset{\cdot\cdot}{-}$O(H) and V$\overset{\cdot\cdot}{-}$O(H) are unavailable, in solution there are certain symmetrical references where relative bond strengths can be assigned on an *a priori* basis, according to the bond valence paradigm. Hence, we use these references in our assignments (see Modus Operandi). After assignments for phosphates and the corresponding vanadates are made, PO and VO bond strengths are compared to assess structural differences between the two. The expected frequency changes for vanadates, distorted so as to mimic dissociative as opposed to associative transition states for concerted PO_3^- transfer, also are calculated. The results are used in the accompanying paper (Deng *et al.*, 1993) as a guide for interpreting the observed stretching frequencies for the phosphate groups of phosphoglucomutase and its complexes with glucose phosphates and of a vanadate-based "transition-state analog" complex of phosphoglucomutase. A manuscript in preparation utilizes V$\overset{\cdot\cdot}{-}$O stretching frequencies as a guide in establishing the structure of the glycol–vanadate dimer complex; an Appendix that appears as supplementary material considers what the current approach suggests about long, weak P··O and V··O bonds involving water in the tetrahydroxyphosphonium ion and in dihydrogen vanadate.

EXPERIMENTAL PROCEDURES

"Anhydrous" methanol was obtained from Aldrich and dispensed under N_2 without additional drying. Aqueous solutions of 1 M "Na_2HVO_4" and 1 M "Li_2HVO_4" were obtained by stirring V_2O_5 (Aldrich) with 4.0 equiv of aqueous NaOH or LiOH overnight at room temperature; 1 M "NaH_2VO_4" was obtained by hydrating $NaVO_3$ (Aldrich) overnight at room temperature and removing a small residue of "hydrated V_2O_5" by centrifugation. Samples of NaH_2VO_4 were carefully degassed under vacuum, and oxygen absorption was minimized during Raman spectroscopy, although this step did not appear to be necessary for other vanadates. $(CH_3O)_2VO_2^-$ was obtained by diluting 1 M LiH_2VO_4 to 25 mM in anhydrous methanol; $CH_3OVO_3^{2-}$ was obtained either by adding 6% (v/v) water to the above methanolic solution or by diluting 1 M NaH_2VO_4 to 25 mM in either 94% methanol/water or 90% methanol containing 0.1 N NaOH [*cf.* Ray and Post (1990)].

Dimethyl phosphate was prepared by reaction of the triester (Aldrich) with a 50% excess of aqueous NaOH at room temperature. Monomethyl phosphate, mono- and dianion, were obtained by hydrolysis of methyl phosphodichloridate (Aldrich) in the presence of 1.0 and 2.0 equiv of NaOH, respectively.

^{31}P and ^{51}V NMR spectra were obtained with a 500-MHz Varian VXR 5000 spectrometer with a broad-band tunable probe and a 5-mm sample tube. The spectrometer was operated at 202.3 and 131.5 MHz for ^{31}P and ^{51}V, respectively.

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[4] Badger's relationship (Badger, 1935) and Gordy's equation (Gordy, 1946), on which it is based, are frequently referred to herein. For easy reference, these are

$$k_e = (C_{ij}/r_e)^{1/2} + d_{ij}$$

where r_e and k_e are the equilibrium bond distance and stretching force constant and C_{ij} and d_{ij} are adjustable parameters, and

$$k = aN(\chi_A\chi_B/d^2)^{3/4} + b$$

where N is bond order (herein, bond strength, s), k and d are the same as k_e and d_e in Badger's relationship, χ_A and χ_B are the electronegativities of atoms A and B, and a and b are empirically assigned parameters. In both cases, k is related to vibrational energy by

$$E_n = (n + {}^1/_2)\hbar(k/\bar{m})^{1/2} = h\nu_n$$

where n and $\bar{m}$ are quantum energy level and reduced mass, respectively.

[5] Bond strength usually is referred to in the biochemical literature as bond order. However, in other disciplines, bond order frequently is reserved for the related parameter obtained from quantum mechanics, whose value depends on the basis set chosen *etc.* Hence, bond order is not used herein.

Raman spectra were obtained as described (Yue *et al.*, 1989). Polarization studies were conducted with plane-polarized irradiating laser light using the 514.5-nm line from an argon ion laser at the power level of 100–200 mW; the emitted Raman scattered light was passed through a polarizer oriented either parallel or perpendicular to the plane of the incident light. In some experiments, a half-wave retarder was used to control the polarization of the incident laser light on the sample but without using the polarizer before the spectrometer. No detectable difference was found in the derived depolarization ratio of the observed Raman bands obtained by these two methods.

MODUS OPERANDI

According to the bond valence paradigm (Brown, 1992; Brown & Wu, 1976; Brown & Shannon, 1973), bond strength, s, is exponentially related to measured bond length, r: $s = (r/r_0)^p$, where r_0 and p are empirical parameters that bear some relationship to atomic size (Brown & Shannon, 1973). In crystalline V/O compounds, where r varies widely, Hardcastle and Wachs (1991) showed that vibrational frequency also is logarithmically related to r: $\ln \upsilon = br + c$, where b and c are empirical parameters. By appropriately combining the above two relationships, an equation with two adjustable parameters is obtained that relates values υ to s (since the exponent, p, is considered fixed). For phosphorus oxides this equation is

$$s = (a \ln\{b/\upsilon_\omega\})^{-4.29} \qquad (1)$$

Hence, the challenge is to adjust the a and b parameters so that $\sum s'_{P\ddot{-}O(H)}$ for phosphorus in a series of phosphates in aqueous solution, calculated from measured values of $\upsilon'_{P\ddot{-}O}$ and $\upsilon'_{P\ddot{-}OH}$ by use of the above relationship, lies as close as possible to the valence of phosphorus in phosphates: 5. In this section we briefly outline the procedure used to adjust a and b to accomplish this.

Because the $H_2PO_4^-$ ion exhibits C_{2v} symmetry in solution, according to the bond valence paradigm, $s'_{P\ddot{-}O} = 1.25 + \Delta$ and $s'_{P\ddot{-}OH} = 1.25 - \Delta$, so that $2s'_{P\ddot{-}O} + 2s'_{P\ddot{-}OH} = 5.0$ vu. [A choice of $s'_{P\ddot{-}O} + s'_{P\ddot{-}OH}$ bond valences for the P$\ddot{-}$O and P$\ddot{-}$OH groups of $(H_2PO_4^-)_{aq}$ is possible by determining what value of Δ is consistent with a bond valence sum of 2 and 1 for oxygen and hydrogen, respectively (Brown, 1992), but making such a choice requires that H-bonding to water also be considered. Although this can be done empirically (Brown, 1992; see also Discussion), in our procedure experimental values of υ'_ω for P$\ddot{-}$O and P$\ddot{-}$OH are used to define bond strengths without attempting to make the sum of the bond strengths involving O and H equal to 2 and 1, respectively.] A second "standard", PO_4^{3-}, that has an even higher symmetry also is used to evaluate Δ, since an *a priori* designation of P$\ddot{-}$O strength for this ion also is feasible: 1.25 vu. The chosen value of Δ, 0.11 vu, which also fixes the value of the a/b pair, is that which brings the value of $s'_{P\ddot{-}O}$ for PO_4^{3-} as close as possible to 1.25 vu, without forcing the calculated value of $\upsilon'_{\omega(P\ddot{-}O)}$ to become unreasonably large when $s'_{P\ddot{-}O} = 2.0$ vu; see Results.

A tacit assumption in the above strategy is that values of υ'_ω for P$\ddot{-}$O and P$\ddot{-}$OH are the same (within experimental error) when $s'_{P\ddot{-}O} = s'_{P\ddot{-}OH}$, although there obviously is a difference between P$\ddot{-}$O and P$\ddot{-}$OH in terms of both reduced mass and extent of H-bonding to water. Support for this assumption is provided in the Discussion.

In the case of vanadates, a somewhat different procedure was used. Although fundamental frequencies[3] usually are used in correlations involving bond strength, and are used here for phosphates, the difference between υ_s and υ_a is much smaller for V$\ddot{-}$O bonds of vanadates (Hardcastle & Wachs, 1991) than for P—O bonds of phosphates. Hence, $\upsilon_{s(V\ddot{-}O)} \approx \upsilon_{\omega(V\ddot{-}O)}$, and we use υ'_s for correlations involving vanadates, as did the above authors. (The substantial problem of measuring υ_a, which for vanadates is much weaker in Raman spectra than is υ_s, also contributed to this choice.)

Table I: Symmetrical Raman Stretching Frequencies for V$\ddot{-}$O and P$\ddot{-}$O(H) Groups in Simple Phosphates and Vanadates[a]

	P$\ddot{-}$O or V$\ddot{-}$O		P$\ddot{-}$O(H)		
species	υ'_s[b] (cm^{-1})	av υ'_s[c] (cm^{-1})	$\upsilon'_{a(P\ddot{-}O)}$ (cm^{-1})	$\upsilon'_{s(P\ddot{-}OH)}$ (cm^{-1})	$\upsilon'_{a(P\ddot{-}OH)}$ (cm^{-1})
$(HO)_3PO$	1170	1178		895	1009
$(CH_3O)_3PO$	1187				
$[(ClCH_2CH_2O)_3VO]_2$	1007[d]	1007			
$(HO)_2PO_2^-$	1073				
$(CH_3O)_2PO_2^-$	1085	1079	1156	881	943
$(CH_3O)(HO)PO_2^-$	1080				
$(HO)_2VO_2^-$	935	930			
$(CH_3O)_2VO_2^-$	926[e]				
$HOPO_3^{2-}$	988	984			
$CH_3OPO_3^{2-}$	980		1082	854	
$HOVO_3^{2-}$	870	870			
$CH_3OVO_3^{2-}$	870[f]				
PO_4^{3-}	934	934	1010		
VO_4^{3-}	823	823			
$(HO)_4P^+$				897	

[a] When there is no antisymmetric stretching mode, the observed frequency is listed under υ'_s; see footnote 3. [b] Values for H_3PO_4 and for ester anions of H_3PO_4 and for vanadates measured herein except where indicated. [c] Average values for acids and the corresponding esters. [d] From Priebsch and Rehder (1990); measured in neat solution in the absence of water: see footnote 5. [e] In dry methanol or methanol containing 2–3% water. This band is split in the diester, with the two lobes of the bifurcated peak centered at about 910 and 940 cm^{-1}, respectively. When [^{18}O]vanadate is used, both lobes of the band shift to a lower frequency by about 42 cm^{-1}. [f] In methanol containing 5–20% water.

The range of $\upsilon_{s(V\ddot{-}O)}$ and $s_{V\ddot{-}O}$ values for vanadium oxides correlated by eq 2 (Hardcastle and Wachs, 1991) is impressive:

$$s_{V\ddot{-}O} = [0.2912 \ln\{21349/\upsilon_{s(V\ddot{-}O)}\}]^{-5.1} \qquad (2)$$

However, when $\upsilon_{s(V\ddot{-}O)}$ is replaced by $\upsilon'_{s(V\ddot{-}O)}$ for aqueous VO_4^{3-}, the calculated value of $s'_{V\ddot{-}O}$ is 5% too large; see Results. In addition, values of $s'_{V\ddot{-}O}$ calculated via eq 2 with data for other vanadates require that $s'_{V\ddot{-}OH}$ be considerably less than 1.0 vu if $\sum s'_{V\ddot{-}O(H)}$ is to be 5.0 vu. Because of this problem, and since our interest is in a much narrower range of bond lengths, bond strengths, and vibrational frequencies than examined by Hardcastle and Wachs, the two adjustable parameters in their equation (eq 2) were altered so that in the range 690 cm^{-1} $\leq \upsilon'_{s(V\ddot{-}O)} \leq$ 1030 cm^{-1} ($1.0 \leq s'_{V\ddot{-}O} \leq 1.8$) calculated values of $s'_{V\ddot{-}O}$ are reduced by factors of approximately 1.05:

$$s'_{V\ddot{-}O} = [0.300 \ln\{20000/\upsilon'_{s(V\ddot{-}O)}\}]^{-5.1} \qquad (3)$$

RESULTS

Throughout this paper, parameters whose values apply to solutions (primarily aqueous solutions), as opposed to the crystal phase, are marked with a prime. The relationships of Brown and Wu (1974) were used to calculate bond strength from atomic distances, where available, and vise versa when bond strength could be estimated as in the Modus Operandi.

Although values of the symmetric stretching mode, υ'_s, for phosphoric acid (H_3PO_4) and its anions have been measured many times [*cf.* Zwick *et al.* (1989)], the symmetrical stretching frequencies in Table I were remeasured for

Table II: Bond Strength of Phosphorus–Oxygen Bonds in Phosphoric Acid and Its Anions[a]

species	$\nu'_{\omega(\text{P}\doteq\text{O})}$[b] (cm^{-1})	$\nu'_{\omega(\text{P}\doteq\text{OH})}$[b] (cm^{-1})	$s'_{\text{P}\doteq\text{O}}$ (vu)	$s'_{\text{P}\doteq\text{OH}}$ (vu)	summed bond strengths[c] (vu)
H_3PO_4	1170	972	1.43 (1.49)	1.21 (1.19)	5.06 (5.06)
$H_2PO_4^-$	1115	912	1.37 (1.39)	1.15 (1.17)	5.04 (5.12)
HPO_4^{2-}	1052	854	1.30 (1.285)	1.09 (1.15)	4.99 (5.01)
PO_4^{3-}	991		1.235 (1.23)		4.94 (4.92)

[a] Values calculated by use of eq 4 plus the fundamental frequencies in columns 2 and 3. Values in parentheses, columns 4–6, calculated with eq 5 and values of $\nu'_{s(\text{P}\doteq\text{O(H)})}$ (columns 3 and 5, Table I). [b] From columns 3–6, Table I. [c] $(4 - n)s'_{\text{P}\doteq\text{O}} + ns'_{\text{P}\doteq\text{OH}}$, where n is the number of P$\doteq$OH groups.

comparison with those of vanadates obtained under the same conditions (although observed differences with the earlier values proved to be insignificant). The values of ν'_a used to calculate ν'_ω (Table II) also were measured, and a distinction between ν'_s and ν'_a was made on the basis of polarization studies (see footnote 3 for definitions of vibrational modes). In the case of vanadates, the presence of oligomers (see footnote 2) was circumvented by employing dilute solutions (1–25 mM) and spectral difference techniques. Thus, for $(CH_3O)_2VO_2^-$, $CH_3OVO_3^-$, and $HOVO_3^{2-}$, conditions were selected with the aid of ^{51}V NMR spectroscopy so that essentially only the indicated species were present (≥95%). But with $(HO)_2VO_2^-$, a significant amount of $V_4O_{12}^{4-}$, and to a lesser extent $H_2V_2O_7^-$, was present in all samples examined [concentration ≥1 mM; *cf.* Heath and Howarth (1982)]. However, the $>VO_2^-$ group serves as the basic unit in the structure of $(HO)_2VO_2^-$, as well as that of both oligomers; hence, ν'_s for this unit should be essentially the same in all three species. In fact, the V$\doteq$O frequency in the Raman difference spectrum (solution minus solvent) decreased only by about 10 cm^{-1} as the total vanadate concentration was reduced from 25 mM, where $V_4O_{12}^{4-}$ is by far the most abundant species, to 1 mM, where $(HO)_2VO_2^-$ represents the major species [as indicated by ^{51}V NMR: *cf.* Heath and Howarth (1981)]. Hence, the frequency given for $(HO)_2VO_2^-$ undoubtedly is close to its true value.

Relationship of Fundamental Frequency to Bond Strength for Phosphates in Aqueous Solution. Initial values of the adjustable *a* and *b* parameters in the frequency–bond strength relationship of eq 1 were selected on the basis of the ν'_ω values in Table II and the procedure described in Modus Operandi. After a minor adjustment to bring the summed bond strengths for each of the four species as close as possible to 5.0 vu, the selected *a*/*b* pair (eq 4)produces an $s'_{\text{P}\doteq\text{O}}$ value of 1.235 vu

$$s'_{\text{P}\doteq\text{O(H)}} = [0.1923 \ln\{140000/\nu'_{\omega(\text{P}\doteq\text{O(H)})}\}]^{-4.29} \quad (4)$$

for PO_4^{3-} (instead of 1.25 vu, as originally assumed) plus $s'_{\text{P}\doteq\text{O}}$ and $s'_{\text{P}\doteq\text{O(H)}}$ values of 1.37 and 1.15 vu for the monoanion (instead of 1.14 and 1.36 vu as originally assumed). These give summed bond strengths of 4.94 and 5.04 vu for phosphorus in the trianion and monoanion, respectively, and a calculated value of $\nu'_{\omega(\text{P}=\text{O})}$ equal to 1680 cm^{-1}.[6] Values of $s'_{\text{P}\doteq\text{O}}$ and $s'_{\text{P}\doteq\text{OH}}$ for the two remaining members of the series, $H_3PO_4 \rightarrow PO_4^{3-}$, obtained with eq 4 and the corresponding values of ν'_ω, columns 2 and 3, Table II, are given in columns 4 and 5 of the same table. The average of the summed values of $s'_{\text{P}\doteq\text{O(H)}}$ for all four species, column 6, Table II, is close to 5.0 vu [actually 5.01 ± 0.05 (SD)], which was our objective. Hence, in essence eq 4 simply serves as a vehicle for interpolating bond strengths in the approximate range 1.1 vu $\leq s'_{\text{P}\doteq\text{O(H)}} \leq$ 1.5 vu, using the relationships described in Modus Operandi.

Relationship of Symmetrical Stretching Frequency to Bond Strength for Phosphates in Aqueous Solution. To determine whether the more readily obtained symmetrical stretching frequency, ν'_s, can be substituted for ν'_ω in defining a frequency–bond strength relationship for the phosphates in Table I, the procedure described in Modus Operandi was repeated using ν'_s. The alternative constants obtained are given in eq 5. Values in parentheses in columns 4–6, Table II,

$$s'_{\text{P}\doteq\text{O(H)}} = [0.1792 \ln\{190000/\nu'_{s(\text{P}\doteq\text{O(H)})}\}]^{-4.29} \quad (5)$$

were calculated with this equation plus values of ν'_s (from Table I). Since the average difference in the values of $s'_{\text{P}\doteq\text{O(H)}}$ calculated with ν'_s as opposed to ν'_ω is only about 0.025 vu, eq 5 holds reasonably well over the range of 1.1 vu $\leq s_{\text{P}\doteq\text{O(H)}} \leq$ 1.5. vu and probably extends at least 0.1 vu on both sides of this range. In other words, eqs 2 and and 5 are of approximately equal value for assessing bond strengths and thus internal bonding in simple phosphates. However, values obtained with ν_ω are considered more reliable. This correspondence between bond strength for phosphates estimated on the basis of ν'_s and ν'_ω places the analogous calculation involving vanadates, for which ν'_a was not measured, on an even firmer foundation (see below).

Gordy-Style Relationship between Symmetrical Stretching Frequency and Bond Strength for Phosphates in Aqueous Solution. Figure 1 shows the relationship between the bond strength of P$\doteq$O(H) groups in phosphoric acid and its anions, calculated by using either ν'_ω (eq 4) or ν'_s (eq 5) and displayed in terms of a Gordy-style relationship (1946) involving ν_ω^2 (△) or ν_s^2 (○) and $s_{\text{P}\doteq\text{O(H)}}$. In both cases, the fit is reasonable. Hence, a similar set of bond strengths that satisfy the chosen criteria could have been developed on the basis of an assumed linear relationship between ν'^2_ω and $s'_{\text{P}\doteq\text{O(H)}}$, as in Gordy's equation, by using arbitrary parameters. Thus, the linearity of Figure 1 plots simply indicates that in aqueous solutions of inorganic phosphate $(4 - n)(\nu'_{\omega(\text{P}\doteq\text{O})})^2 + n(\nu'_{\omega(\text{P}\doteq\text{OH})})^2$ is approximately constant (±3% SD), where n is the number of P–OH groups.

Relationship of Symmetrical Stretching Frequency to Bond Strength for Vanadates in Aqueous Solution. Since bond strengths for phosphate are essentially the same when estimated by using values of either ν'_s or ν'_ω, and since using ν'_s suffices for estimating $s_{\text{V}\doteq\text{O}}$ in the crystal phase (Hardcastle & Wachs, 1990), eq 3 (Modus Operandi) plus the values of ν'_s in Table I were used to obtain the $s'_{\text{V}\doteq\text{O}}$ values in Table III.[7] Values of $s'_{\text{V}\doteq\text{OH(R)}}$ were calculated as $5.0 - \Sigma s'_{\text{V}\doteq\text{O}}$.[8]

Figure 1 (□) displays a Gordy-style plot involving $(\nu'_s)^2$ for vanadates. A comparison of this plot with that for phosphate (○) shows that a $(\nu'_s)^2$ relationship of this type involving a *single* set of arbitrary parameters cannot relate the stretching

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[6] The calculated frequency for $\nu'_{\omega(\text{P}=\text{O})}$ from eq 4 is significantly higher than that reported for any known P$\doteq$O group [1415 cm^{-1} for F_3PO; *cf.* Nyquist and Potts (1972)]. However, because of the difference in electronegativities of P and O, a "true" double bond is not expected in any compound, and in F_3PO, the bond distance [1.436 Å; *cf.* Corbridge (1990)] corresponds with a bond strength only of about 1.7 vu. But the choice of values for $s'_{\text{P}\doteq\text{O}}$ and $s'_{\text{P}\doteq\text{OH}}$ for $H_2PO_4^-$ (and thus the related *a*/*b* values) does not depend critically on the precise value selected for the maximum possible $\nu'_{s(\text{P}=\text{O})}$. Thus, only a small additional increase in the chosen value of $s'_{\text{P}\doteq\text{OH}}$ (plus a small decrease in $s'_{\text{P}\doteq\text{O}}$) makes the maximum value for $\nu'_{s(\text{P}=\text{O})}$ too large for consideration: >2500 cm^{-1}. At the opposite extreme, *a*/*b* pairs involving significantly smaller values of $s'_{\text{P}\doteq\text{OH}}$ and significantly larger values of $s'_{\text{P}\doteq\text{O}}$ provide a summed bond strength for P of less that 4.8 vu for PO_4^{3-}. These two limits thus essentially eliminate subjective choices.

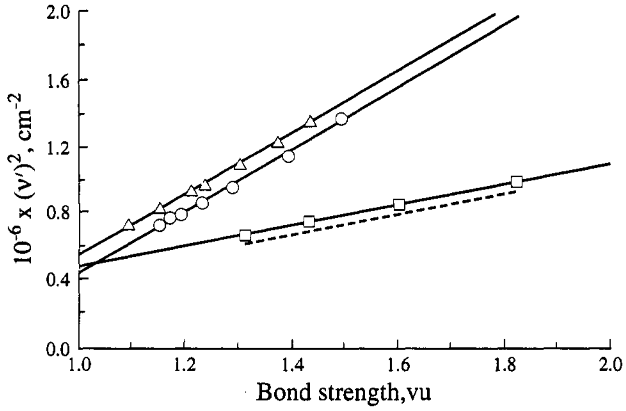

FIGURE 1: Plots showing the relationship between measured values of $(\upsilon')^2$ and bond strength calculated for $\mathrm{P\underline{\cdot\cdot}O(H)}$ bonds of phosphoric acid and its anions and for $\mathrm{V\underline{\cdot\cdot}O}$ bonds of the vanadates in Table I: (△) values for $s'_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ calculated by using $\upsilon'_{\omega(\mathrm{P\underline{\cdot\cdot}O(H)})}$ for phosphoric acid and its anions (Table II) and eq 4; (○) values for $s'_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ calculated with $\upsilon'_{s(\mathrm{P\underline{\cdot\cdot}O(H)})}$ for phosphoric acid and its anions (Table I) and eq 5; (□) values for $s'_{\mathrm{V\underline{\cdot\cdot}O}}$ calculated with average values of $\upsilon'_{s(\mathrm{V\underline{\cdot\cdot}O})}$ (Table I) and eq 3. Regression lines for all three plots were fit to the following Gordy-style relationship (1946): $(\upsilon')^2 = c(s' + d)$. Values of c and d, together with the standard error of the estimate, are as follows: (△) $c = (1.88 \pm 0.03) \times 10^6$, $d = -0.71 \pm 0.02$; (○) $c = (1.90 \pm 0.04) \times 10^6$, $d = -0.768 \pm 0.04$; (□) $c = (0.69 \pm 0.01) \times 10^6$, $d = -0.26 \pm 0.02$. The dashed-line plot for $s'_{\mathrm{V\underline{\cdot\cdot}O}}$ was obtained directly from the Hardcastle–Wachs relationship (eq 2).

Table III: Bond Strength of Vanadium–Oxygen Bonds in Simple Ester/Anions of Vanadic Acid[a]

species	$s'_{\mathrm{V\underline{\cdot\cdot}O}}$ (vu)	required $s'_{\mathrm{V\underline{\cdot\cdot}OH(R)}}$[b] (vu)
$[(\mathrm{ClCH_2CH_2O})_3\mathrm{VO}]_2$	1.74 (1.82)	1.09
$(\mathrm{HO})_2\mathrm{VO_2}^-/(\mathrm{CH_3O})_2\mathrm{VO_2}^-$	1.53 (1.60)	0.97
$\mathrm{HOVO_3}^{2-}/\mathrm{CH_3OVO_3}^{2-}$	1.37 (1.43)	0.89
$\mathrm{VO_4}^{3-}$	1.25 (1.31)	

[a] Calculated by use of eq 3 plus average values of υ'_s from column 3, Table I; values in parentheses calculated by use of eq 2. [b] Value required such that $(4 - n)s'_{\mathrm{V\underline{\cdot\cdot}O}} + ns'_{\mathrm{V\underline{\cdot\cdot}OH(R)}} = 5.0$ vu, where n is the number of $\mathrm{V\underline{\cdot\cdot}OH(R)}$ bonds; see footnote 8.

frequencies of tetrahedral phosphates and vanadates in aqueous solution, even over a narrow range of bond strengths.[9]

DISCUSSION

As is noted in the introduction, a solution version of the network paradigm of chemical bonding in inorganic crystals (Brown, 1992) can be used to approximate bond valences for $\mathrm{P\underline{\cdot\cdot}O(H)}$ in phosphates by employing a widely applicable data base. Our approach differs from Brown's in that we use measured vibrational frequencies for $\mathrm{P\underline{\cdot\cdot}O(H)}$ bonds to establish a spectroscopic bond strength pattern for these compounds, although our results are scaled in such a way that bond strength and bond valence values should be the same. We use this approach because our goal is to provide a way of experimentally evaluating $s_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ for a phosphate group when its environment is not known. However, for the three species where the network paradigm works best, $\mathrm{H_3PO_4}$, $\mathrm{HPO_4}^{2-}$, and $\mathrm{PO_4}^{3-}$, our bond strengths and Brown's bond valences are similar (I. D. Brown, personal communication).[10] (In the case of phosphate esters, the agreement becomes increasingly unsatisfactory as the number of methyl groups increases and the net charge on the anion decreases; thus, the use of the solution version of the bond valence paradigm may be limited to small, highly charged anions.)

The picture of phosphate that emerges from the calculated values of $s'_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ in Table II is both old and new. Thus, it has been known for years that the difference between geminal $\mathrm{P\underline{\cdot\cdot}OH}$ and $\mathrm{P\underline{\cdot\cdot}O}$ bonds in many crystalline phosphates [*cf.* Corbridge (1974, 1990)] is much smaller than one might expect on the basis of compounds such as carboxylic acids (Pauling, 1960). Moreover, in aqueous solution, stretching frequencies for $\mathrm{P\underline{\cdot\cdot}OH}$ and $\mathrm{P\underline{\cdot\cdot}O}$ are "bunched" together relative to expected differences. The calculated values of 1.15 and 1.37 vu, respectively, for $\mathrm{P\underline{\cdot\cdot}OH}$ and $\mathrm{P\underline{\cdot\cdot}O}$ bond strengths in aqueous $(\mathrm{HO})_2\mathrm{PO_2}^-$ (Table II) simply provide an estimate of how similar these $\mathrm{P\underline{\cdot\cdot}O}$ and $\mathrm{P\underline{\cdot\cdot}OH}$ bonds actually are. This estimate differs significantly from what would be expected from the simple canonical structures that frequently are used to represent phosphates. In the case of $\mathrm{H_3PO_4}$, the value for $s'_{\mathrm{P\underline{\cdot\cdot}O}}$, 1.43 vu, can be compared with the calculated bond order of 1.5 for the hypoethetical phosphine oxide, $\mathrm{H_3PO}$, where the bond order of $\mathrm{P\underline{\cdot\cdot}O}$ should be larger than in $(\mathrm{HO})_3\mathrm{PO}$.[11] From an alternative standpoint, the above difference in $s'_{\mathrm{P\underline{\cdot\cdot}O}}$ and $s'_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ in $\mathrm{H_2PO_4}^-$ is equivalent to a difference in bond length of only about 0.06 Å, which is less than 4% of the single bond distances of 1.62 Å (Brown & Wu, 1976). [The Appendix, available as supplementary material, considers what our approach suggests about the structure of the tetrahydroxyphosphonium ion, $\mathrm{P(OH)_4}^+$, produced by protonation of phosphoric acid in stronger acids, such as $\mathrm{H_2SO_4}$ and $\mathrm{HClO_4}$.]

The values of $s'_{\mathrm{P\underline{\cdot\cdot}O(H)}}$ in Table II are not unique from the standpoint that bond strength can be defined in different ways. But if one adopts an alternative definition that, for example, allows the bond strength for $\mathrm{P\underline{\cdot\cdot}O}$ and $\mathrm{P\underline{\cdot\cdot}OH}$ in $\mathrm{H_2PO_4}^-$ to differ to a substantially larger extent than in Table II, one or the other of two basic concepts assumed here ***must be discarded***: either the summed bond strengths for P(*V*) must differ substantially from 5.0 or vibrational frequency and bond strength must be unrelated in aqueous solution. Neither of these alternatives seems palatable.

Ideally, different frequency–bond strength relationships should be used for $\mathrm{P\underline{\cdot\cdot}O}$ and $\mathrm{P\underline{\cdot\cdot}OH}$ bonds, since $(\bar{m})^{1/2}$ for $\mathrm{P\underline{\cdot\cdot}OH}$ is about 2% larger than for $\mathrm{P\underline{\cdot\cdot}O}$. However, both the number and range of the points available for scaling are too

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[7] Entry 3, Table I, should not be excluded from the series under consideration *because* it is a dimer, since dimer formation has little effect on the bond strength of the $\mathrm{V\underline{\cdot\cdot}O}$ group (*cf.* accompanying paper: Deng *et al.*, 1993). Whether or not it should be excluded because the stretching frequency was measured in an environment quite different from the other vanadates is a different question for which we have no easy answer.

[8] True values of $s'_{\mathrm{V\underline{\cdot\cdot}OH(R)}}$ likely are ≥ 1. Those in the right-hand column of Table III are calculated by using (a modified form of) an equation that describes a much larger data base, where maximizing generality was of greater importance than maximizing accuracy for a single type of compound within that data base. Even after modification as above, this equation seems to provide values of $s'_{\mathrm{V\underline{\cdot\cdot}O}}$ for vanadic acid derivatives that are too large by several percent, thus producing values of $s'_{\mathrm{V\underline{\cdot\cdot}OH(R)}}$ that are too small.

[9] According to Gordy's relationship (see footnote 4), the slopes of the plots in Figure 1 for phosphates and vanadates, $\partial(\upsilon')^2/\partial s$, are equal to $c(\chi_A\chi'_B/d^2)^{3/4}/\bar{m}$. From this relationship, the slope ratio for phosphates and vanadates in Figure 1 should be 1.58, instead of 2.96 cm^2/vu. In addition, in Gordy's equation the ratio of the y-intercepts for the two plots is equal to the inverse ratio of $\bar{m}$-values. Again, this is not the case: 3.9 (observed) versus 1.22 cm^2/vu (expected).

[10] The solution version of the bond valence paradigm provides the following bond valence assignments: $\mathrm{P\underline{\cdot\cdot}O}$ in $\mathrm{PO_4}^{3-}$, 1.25 vu; $\mathrm{P\underline{\cdot\cdot}O}$ and $\mathrm{P\underline{\cdot\cdot}OH}$ in $\mathrm{HPO_3}^-$, 1.34 and 0.98 vu, respectively; $\mathrm{P\underline{\cdot\cdot}O}$ and $\mathrm{P\underline{\cdot\cdot}OH}$ in $\mathrm{H_3PO_4}$, 1.4 and 1 .2 vu, respectively. (Bond valence assignments for $\mathrm{H_2PO_4}^-$ are ambiguous: I. D. Brown, personal communication.) The above values can be compared with those in Table II.

[11] We assume that it is reasonable to relate the distances calculated with various 3-21G, 6-31G, or DZ basis sets (Streitweiser *et al.*, 1987) to bond order by using the empirical relationship of Brown and Wu (1976).

limited to justify separate treatments. In theory, the net effect of a single fit is to increase the calculated bond strength of P$\underline{\cdot\cdot}$O and decrease that of P$\underline{\cdot\cdot}$OH in $H_2PO_4^-$ by about 1% each. In H_3PO_4 and HPO_4^{2-} the effect would be increased to about 1.5%.

In the case of vanadates (Table III), there is a substantially greater difference between the bond strength of V$\underline{\cdot\cdot}$O relative to V$\underline{\cdot\cdot}$OH groups than for P$\underline{\cdot\cdot}$O relative to P$\underline{\cdot\cdot}$OH groups (Table II) in anions with the same net charge. Thus, V$\underline{\cdot\cdot}$O is substantially closer to a double bond in such species than is P$\underline{\cdot\cdot}$O whereas $s'_{\mathrm{V\underline{\cdot\cdot}OH}}$ and $s'_{\mathrm{P\underline{\cdot\cdot}OH}}$ differ to a smaller extent.[8] This conclusion is in accord with that of Krauss and Basch (1992), based on molecular orbital calculations involving one vanadate/phosphate pair.

In their study of bond valences in a group of crystalline vanadium oxides that included several vanadates, Hardcastle and Wachs (1991) found that the diatomic approximation, which considers the crystal as a collection of independent (harmonic) oscillators, provides a good correlation between stretching frequency and bond valence. To the extent that this approximation holds, ν_a can be ignored and measured values of ν_s (instead of calculated values of ν_ω) can be used to evaluate bond strength. For aqueous solutions of vanadates, the more or less equivalent statement is that, since ν'_s and ν'_a are not substantially different, $\nu'_\omega = \nu'_s$. Hence, determining whether ν'_s for phosphates can be substituted for ν'_ω to evaluate bond strength relationships is of substantial practical interest to biochemists, since it is difficult to measure ν'_a for dilute solutions of phosphates via Raman spectroscopy because of the low cross section for phosphates. Whether or not such a substitution is feasible for the simple phosphates considered here depends on the magnitude of the difference between ν'_s and ν'_a within an empirical as opposed to a theoretical context. In fact, the comparison of bond strength estimates for phosphates obtained by using $\nu'_{s(\mathrm{P\underline{\cdot\cdot}O(H)})}$ instead of $\nu'_{\omega(\mathrm{P\underline{\cdot\cdot}O(H)})}$ (○ and △, respectively, Figure 1) suggests that the differences are insignificant. However, since the similarity in calculated bond strengths obtained by using ν'_s instead of ν'_ω is somewhat surprising from a theoretical standpoint, and has been verified only for inorganic phosphate and its methyl esters, eq 5 should be used for other phosphate esters with some caution. In addition, because of the possibility of normal mode coupling, eq 5 is not intended for use in interpreting small differences in ν'_s values for phosphate esters with different R groups, although *changes* in ν'_s produced by environmental differences likely can be interpeted reasonably for a variety of phosphate esters.

A second caveat is provided by the observation that a Gordy-style relationship with a singlet set of arbitrary parameters cannot relate the stretching frequencies of tetrahedral phosphates and vanadates in aqueous solution, even over a narrow range of bond strengths (*cf.* footnote 8). Hence, although the P$\underline{\cdot\cdot}$O(H) and V$\underline{\cdot\cdot}$O bonds of both phosphates and vanadates, respectively, seem to act like diatomic oscillators, this conclusion must rest on strictly empirical grounds.

The primary motivation for this study was to provide a basis for interpreting the Raman spectra of phosphates and vanadates bound to enzymes, where both covalent and noncovalent interactions must be involved, as well as Raman spectra of model vanadates whose solution structure is not established. In such studies, one of which is described in the accompanying paper (Deng *et al.*, 1993), knowing the relationship between P$\underline{\cdot\cdot}$O or V$\underline{\cdot\cdot}$O stretching frequency and bond strength can provide critical insights. For example, in the case of phosphoglucomutase the binding of glucose 1-phosphate 6-vanadate to give a putative transition-state analog complex is nearly 10^6-fold stronger than binding of the structurally similar glucose 1,6-bisphosphate. Whereas the difference in P$\underline{\cdot\cdot}$O and V$\underline{\cdot\cdot}$O bond lengths noted in the introduction might provide a partial rationale for this binding difference, it seems likely that most of the difference should be rationalized in terms of properties of phosphates and vanadates in an environment that tends to distort them in the direction of the transition state that the enzyme is designed to stabilize. This is reasonable since the most obvious alternative, a difference in binding modes, seems to be ruled out by the observation that the –Glc-1-P portion of both diesters is bound in the "same" way (Ray *et al.*, 1990). According to the results in the accompanying paper (Deng *et al.*, 1993), the binding-induced distortion is much larger for bound vanadate than bound phosphate since, in the complex of the phosphoglucomutase with Glc-1-P-6-V, the characteristic V$\underline{\cdot\cdot}$O stretching frequency is substantially shifted from its solution value whereas the P$\underline{\cdot\cdot}$O stretching frequency in the corresponding complex involving glucose 1,6-bisphosphate is scarcely affected. (The electronic spectrum of bound vanadate also is substantially altered in the above complex, relative to the solution spectrum; Ray & Post, 1990.)

To use such observations as a basis for deducing properties of the transition state requires that binding-induced distortions, in terms of changes in P$\underline{\cdot\cdot}$O and V$\underline{\cdot\cdot}$O bond strength, be related to the changes expected for various types of transition states (see below). To the extent that the P$\underline{\cdot\cdot}$O and V$\underline{\cdot\cdot}$O groups of phosphates and vanadates actually are independent diatomic oscillators, instead of only seeming to behave so over a narrow range, making such a comparison is straightforward once a transition-state analog is identified. In the case of vanadate, the demonstration by Hardcastle and Wachs (1991) that s_{VO} can be approximated by using a single ν_s versus s_{VO} relationship whether vanadium is surrounded by 4, 5, or 6 oxygen ligands provides adequate support for using eq 3 in such comparisons. In the case of phosphate, where no study analogous to that of Hardcastle and Wachs for vanadates has been conducted, any use of eq 5 to rationalize possible binding-induced changes in phosphates must rest on less firm ground (Deng *et al.*, 1993).

The other part of the transition-state analog problem, as it relates to mechanism, is that distinctions between various types of transition states that have been suggested for transfer processing involving the PO_3^- fragment of a phosphate group are significantly blurred. Thus, it is easy to imagine a near continuum of concerted transfer processes, with different degrees of bond breading/bond making in the transition state, that lie between the extremes of stepwise processes where there is a discrete metaphosphate intermediate, on one hand, and a phosphorane-like adduct, on the other [*cf.* Cullis (1987)]. And, from an experimental standpoint, the problem of distinguishing between transition states that are part of this continuum is further exacerbated in an enzymic reaction when there are substantial differences in the chemistry of the PO_3^- donor and acceptor groups. Since, in the case of phosphoglucomutase, the character of these groups, $\mathrm{Ser}^{116}\mathrm{O}\gamma$, 6-*O*-Glc-1-P, and 1-*O*-Glc-6-P, is similar, in contemplating possible transition states within the above continuum, it seems reasonable to focus on those that are symmetrical, or nearly so, and to group these in terms of the summed strengths of the donor/acceptor oxygen bonds to phosphorus in the transition state, *i.e.*, apical transition-state bonds [*cf.* Hengge and Cleland (1991)], although other criteria also can be factored in. If the sum of the bond strengths for these apical bonds is much less than 1, *e.g.*, 0.2, a largely dissociative transition state is indicated, as for model reactions involving

Table IV: Estimates of the Symmetrical $\mathrm{P\overset{..}{-}O}$ and $\mathrm{V\overset{..}{-}O}$ Stretching Frequencies in Hypothetical Dianionic Pentacoordinate Complexes with C_{3v} Symmetry

summed bond strengths[a] (vu)			
apical bonds	equatorial bonds	$\nu'_{s(\mathrm{P\overset{..}{-}O})}$[b] ($\mathrm{cm^{-1}}$)	$\nu'_{s(\mathrm{V\overset{..}{-}O})}$[c] ($\mathrm{cm^{-1}}$)
0.15	4.85	1295	965
0.5	4.5	1210	925
1.0	4.0	1065	860
1.5	3.5	900	790

[a] Taken as 5.0; see Discussion. [b] Calculated with eq 5. [c] Calculated with eq 3.

dianionic phosphate esters (Herschlag & Jencks, 1990, and references therein). Since in an enzymic reaction, binding interactions may alter the course of the reaction, it seems possible that the transition state could acquire added associative character. Precisely when it becomes reasonable to describe such a transition state as associative is problematic, but, in the present case, if the sum of the donor/acceptor bond strengths in the transition state becomes 1, the transition state is as associative as the classical $\mathrm{S_N2}$ process at a saturated carbon atom. In theory, as the summed apical bond strengths in the transition state become significantly greater than 1, the transition state would acquire adduct-like character. Such character would be extensive at a value of 1.5, since the related sum for a true phosphorane (neutral) is only about 1.7 [*cf.* the accompanying paper: Deng *et al.* (1993)].

On the basis of the above consideration, Table IV shows the expected $\mathrm{V\overset{..}{-}O}$ stretching frequencies for various types of symmetrical, pentacoordinate complexes involving a dianionic vanadate ester. If such vanadate complexes serve as mimics for the concerted transition states outlined above, the summed bond strengths for apical groups in these complexes would be 0.15 vu (truly dissociative), 0.5 vu (partially associative), 1.0 vu (associative, or $\mathrm{S_N2}$-like), and 1.5 vu (adduct like, bordering on stepwise). In these cases, the sum of $\mathrm{V\overset{..}{-}O}$ bond strengths involving the nonbridging oxygens should be 4.85, 4.5, 4.0, and 3.5 vu, respectively. Related expectations also are shown for a phosphate ester dianion, although it is unlikely that bonding patterns of this type would be observed for a phosphate group in the ground state.

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SUPPLEMENTARY MATERIAL AVAILABLE

An appendix containing observations about the structure of the tetrahydroxyphosphonium ion and dihydrogen vanadate and weak P–O and V–O bonds involving water (3 pages). Ordering information is given on any current masthead page.

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